

5 DOUBLE CURRENT COLLECTOR NEGATIVE ELECTRODE
DESIGN FOR ALKALI METAL ION ELECTROCHEMICAL CELLS

CROSS REFERENCE TO RELATED APPLICATION

This application claims priority based on
provisional application Serial No. 60/249,688, filed
10 November 17, 2000.

BACKGROUND OF THE INVENTION

This invention relates to the conversion of
chemical energy to electrical energy. In particular,
the present invention relates to a new negative
15 electrode design having an anode active material
sandwiched between two current collectors with an anode
material capable of intercalating and de-intercalating
the anode active material in contact with the opposite
sides of the current collectors. The present negative
20 electrode design is useful for high discharge rate
secondary cells, such as those powering an implantable
medical device.

SUMMARY OF THE INVENTION

Secondary electrochemical cells are typically built
25 in a discharged state having a negative electrode of a
carbonaceous material and a positive electrode of a
lithiated material. A reverse potential is then applied
to the cell to cause lithium ions at the positive
electrode to migrate through the electrolyte and
30 intercalate into the carbonaceous anode material. The
cell is then discharged in a normal manner.

Graphitic forms of carbon are generally preferred
for the anode material because they exhibit acceptable
cycling capability and good reversible capacity,
35 especially during initial charge and discharge cycles.

5 While graphite is commonly used, there are other carbonaceous materials which have better reversible capacities. One in particular is hard carbon. This material has excellent cycling characteristics, but suffers from a relatively large initial irreversible
10 capacity.

Therefore, according to the present invention, a secondary cell is constructed having a "sacrificial" piece of alkali metal as a portion of the negative electrode along with an alkali metal intercalation and de-intercalation material, such as a carbonaceous anode material. In the case of hard carbon, the sacrificial alkali metal is preferably a piece of lithium metal and is sized to compensate for the initial irreversible capacity of this anode material. After the cell is activated with an electrolyte, the lithium metal automatically intercalates into the hard carbon anode material. That way, the sacrificial lithium metal compensates for the generally unacceptable irreversible capacity of hard carbon. The superior cycling longevity of hard carbon now provides a secondary cell of extended use beyond that known for conventional secondary cells having only graphitic anode materials.

Accordingly, one object of the present invention is to improve the cycling performance of lithium ion cells by providing a new concept in negative electrode design. Further objects of this invention include providing a cell design for improving the capacity and utilization efficiency of lithium-containing secondary cells.

These and other objects of the present invention will become increasingly more apparent to those skilled

5 in the art by reference to the following description.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The electrochemical cell of the present invention is of a secondary, rechargeable chemistry. The cell 10 comprises an anode active metal selected from Groups IA, IIA and IIIB of the Periodic Table of the Elements, including lithium, sodium, potassium, etc.

In conventional secondary electrochemical systems, the anode or negative electrode comprises an anode 15 material capable of intercalating and de-intercalating the anode active material, such as the preferred alkali metal lithium. Typically, the anode material of the negative electrode comprises any of the various forms of carbon (e.g., coke, graphite, acetylene black, carbon 20 black, glassy carbon, etc.) which are capable of reversibly retaining the lithium species. Graphite is particularly preferred in conventional secondary cells. "Hairy carbon" is another particularly preferred conventional material due to its relatively high 25 lithium-retention capacity. "Hairy carbon" is a material described in U.S. Patent No. 5,443,928 to Takeuchi et al., which is assigned to the assignee of the present invention and incorporated herein by reference.

30 However, it is known that graphitic forms of carbon do not possess as high of a reversible capacity as hard carbon. Hard carbon, defined as non-graphitizable carbon material, has two to four times as much reversible capacity as graphite. Hard carbon is 35 typically prepared by firing an appropriate organic

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5 cursor to temperatures between 700°C and 1,200°C. Hard
carbons typically exhibit excellent cyclability and high
reversible capacity. The current state of the art,
i.e., graphite, is theoretically limited to a capacity
of 372 mAh/g, while hard carbons exhibit capacities of
10 400 mAh/g or more. This means that a secondary cell
built with hard carbon as the anode material can be
charged and discharged, or cycled, two to four times as
much as a secondary cell built with a graphitic form of
anode material. The improvement in cycle life is based
15 on the dimensional stability of hard carbon during
lithium intercalation and de-intercalation. This means
that a secondary cell built with hard carbon as the
anode material has potentially higher capacity than a
secondary cell built with a graphitic form of anode
20 material.

On the other hand, the main reason hard carbon is
not used more frequently in secondary cells is because
it suffers from large initial cycle irreversible
capacity relative to graphite. This irreversible
25 capacity must be compensated for by the addition of
cathode active material to the cell which, in turn,
lowers the cell's capacity.

For this reason, the negative electrode of the
present secondary cells is built in a double screen
30 configuration having a "sacrificial" piece of alkali
metal, preferably lithium, sandwiched between two
current collectors. A carbonaceous material or a
material capable of intercalation and de-intercalation
of the alkali metal contacts the opposite side of at
35 least one, and preferably both, of the current

5 collectors. The purpose of the sacrificial alkali metal
is to compensate for the irreversible capacity of the
intercalation and de-intercalation material, for example
hard carbon, versus graphite. One embodiment of the
present negative electrode has the following
10 configuration:

hard carbon/current collector/lithium/current
collector/hard carbon.

With this double current collector electrode
design, the amount of lithium metal is adjusted to
15 precisely compensate for the irreversible capacity of
the hard carbon. Upon activating the cell with an ion-
conductive electrolyte, the alkali metal migrates into
the hard carbon resulting in complete consumption of the
alkali metal. The absence of the alkali metal in the
20 cell preserves the desirable safety and cycling
properties of the intercalation negative and positive
electrodes. Therefore, the present negative electrode
preferably having lithium metal sandwiched between two
current collectors which are further sandwiched between
25 two hard carbon structures has a significantly higher
volumetric and/or gravimetric energy density than a
conventional negative electrode of a carbonaceous
material contacted to a single current collector.

30 Regardless of the carbonaceous nature or makeup of
the anode material, fibers are particularly
advantageous. Fibers have excellent mechanical
properties which permit them to be fabricated into rigid
electrode structures that are capable of withstanding
degradation during repeated charge/discharge cycling.

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5 Moreover, the high surface area of carbon fibers allows
for rapid charge/discharge rates.

The carbonaceous portion of the present negative
electrode for a secondary cell is fabricated by mixing
about 90 to 97 weight percent of the anode material,
10 preferably hard carbon, with about 3 to 10 weight
percent of a binder material, which is preferably a
fluoro-resin powder such as polytetrafluoroethylene
(PTFE), polyvinylidene fluoride (PVDF),
polyethylenetetrafluoroethylene (ETFE), polyamides,
15 polyimides, and mixtures thereof.

This negative electrode admixture is provided on a
current collector such as of a copper, stainless steel,
titanium, tantalum, platinum, gold, aluminum, nickel,
cobalt nickel alloy, highly alloyed ferritic stainless
20 steel containing molybdenum and chromium, and nickel-,
chromium-, and molybdenum-containing alloy foil or
screen by casting, pressing, rolling or otherwise
contacting the admixture thereto.

Another type of anode material useful with the
25 present invention is a metal which can reversibly alloy
with alkali metals. Such metals include, but are not
limited to, Sn, Si, Al, Pb, Zn, and Ag. These alloying
metals demonstrate very high reversible capacities, but
suffer from poor cycling properties because of massive
30 dimensional changes during the alloying process. One
approach which has been used to solve this problem is to
suspend nano-sized particles of them in a matrix of
inactive material. The inactive material is typically
generated by reduction of an oxide of the alloying metal
35 during the first cycle. Examples of oxides include but

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5 are not limited to SnO , SnO_2 , SiO , and $\text{SnO}(\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_y$.
These oxides exhibit good cycling properties and high
reversible capacities, but reduction of the metal oxide
consumes large amounts of alkali metal during the first
charge. Thus, in conventional secondary chemistries,
10 additional cathode active material must be incorporated
into the cell to compensate for this reduction, thereby
reducing cell capacity.

It is, therefore, another preferred embodiment of
the present invention to place a piece of alkali metal
15 between the above metal oxide anode materials. The
amount of alkali metal is chosen to precisely compensate
for the reduction of the metal oxide. Then, upon
activating the cell with an ion-conductive electrolyte,
the alkali metal migrates into the anode material
20 resulting in complete consumption of the alkali metal.
As before, the absence of alkali metal in the cell
preserves the desirable safety and cycling properties of
the anode material, and the resulting cell has capacity
which exceeds that of the current art.

25 Still another preferred embodiment of the present
invention takes advantage of active materials that are
typically used as cathode active materials in primary
cells, but which can not normally be used in
conventional secondary cells. The current art in
30 rechargeable cells typically uses the positive electrode
as the source of alkali metal ions. This prohibits the
use of metal-containing cathode active materials which
do not contain alkali metal ions. Examples of such
metal-containing materials include V_2O_5 , SVO , CSVO , MnO_2 ,
35 TiS_2 , CuO_2 , Cu_2S , FeS , FeS_2 , CF_x , Ag_2O , Ag_2O_2 , CuF ,

5 Ag_2CrO_4 , copper oxide, copper vanadium oxide, and
mixtures thereof. The use of these active materials in
the positive electrode of a secondary cell normally
requires the presence of an alkali metal anode or a pre-
metallated anode material (most desirably carbon). The
10 use of an alkali metal anode is undesirable because of
the previously discussed poor cycling and safety
properties of these materials. Pre-metallated carbon
materials are known in the art, but have never been
commercialized because of difficulties in reliably
15 manufacturing them.

In the present invention, a piece of alkali metal
is used in conjunction with one or more of the
previously described metal-containing materials which
are typically used as cathode active materials in
20 primary cells. In the present invention, the piece of
alkali metal serves as the source of alkali metal ions
and is sandwiched between two layers of one or more of
the above metal-containing materials now serving as an
anode material. The amount of alkali metal is chosen
25 such that it precisely compensates for the reversible
capacity of the anode material. Upon activating the
cell with an ion-conductive electrolyte, the alkali
metal migrates into the anode material resulting in
complete consumption of the alkali metal, which
30 preserves the desirable safety and cycling properties of
the anode material.

Now, it is possible for the positive electrode to
have as its active material any of the above materials
which are described as useful anode materials for the
35 negative electrode of the present invention and which

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5 form an acceptable electrochemical potential with the anode material. As previously described, these materials are not typically used as cathode active materials in secondary cells because they are not lithiated. An exemplary couple would be graphite/Li as
10 a negative electrode and V₂O₅ or SVO as a positive electrode.

As is the case with the above described carbonaceous anode materials, the alloying anode metals and the metal-containing anode materials are formed into a sandwich electrode body for incorporation into an electrochemical cell by mixing one or more of them with one of the above described binder materials. Further, up to about 10 weight percent of a conductive diluent is preferably added to the mixture to improve conductivity.

Suitable materials for this purpose include acetylene black, carbon black and/or graphite or a metallic powder such as powdered nickel, aluminum, titanium and stainless steel. The preferred anode material mixture thus includes a powdered fluoro-polymer binder present at about 1 to 5 weight percent, a conductive diluent present at about 1 to 5 weight percent and about 90 to 98 weight percent of the anode material.

30 Therefore, one exemplary negative electrode has an anode material short circuited to the alkali metal anode active material by parallel connection through the current collectors. The following configuration is exemplary:

first anode material/current collector/alkali metal/current collector/second anode material, wherein the first and second anode materials are either the same

5 or different.

Another embodiment of the present invention has the alkali metal sandwiched between the anode material, in which the anode material is short circuited to the alkali metal by direct contact. This negative electrode
10 has the configuration:

first anode material/current collector/second anode material/alkali metal/third anode material/current collector/fourth anode material, wherein the first, second, third and fourth anode materials are either the
15 same or different.

A third exemplary embodiment of the present invention has the configuration:

anode material/current collector/alkali metal, wherein the anode material faces the positive electrode.

20 More preferred embodiments include the following negative electrode configurations:

hard carbon/current collector/lithium/current collector/hard carbon, or

25 anode material/current collector/lithium/current collector/anode material, wherein the anode material is selected from the group consisting of SnO , SnO_2 , SiO , $\text{SnO}(\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_y$, V_2O_5 , SVO , CSVO , MnO_2 , TiS_2 , CuO_2 , Cu_2S , FeS , FeS_2 , CF_x , Ag_2O , Ag_2O_2 ,
30 CuF , Ag_2CrO_4 , copper oxide, copper vanadium oxide, and mixtures thereof, or

carbonaceous material/current collector/lithium/current collector/carbonaceous material, or

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5 graphite/current
collector/graphite/lithium/graphite/current
collector/graphite.

In a secondary cell, the reaction at the positive
electrode involves conversion of ions which migrate from
10 the negative electrode to the positive electrode into
atomic or molecular forms. The positive electrode
preferably comprises lithiated oxides, sulfides,
selenides, and tellurides of such metals as vanadium,
titanium, chromium, copper, molybdenum, niobium, iron,
15 nickel, cobalt and manganese. Preferred lithiated
oxides include $\text{Li}_x\text{Ti}_5\text{O}_{12}$ (x = 4 to 7), $\text{Li}_{3-x}\text{M}_x\text{N}$ (M = Co,
Ni; x = 0.1 to 0.6), LiNiO_2 , LiMn_2O_4 , LiMnO_2 , LiV_2O_5 ,
 LiCoO_2 , $\text{LiCo}_{0.92}\text{Sn}_{0.08}\text{O}_2$ and $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$. The above-
described alkali metal intercalation and de-
20 intercalation materials such as SVO, CSVO, Ag_2O , Ag_2O_2 ,
 CuF_2 , Ag_2CrO_4 , MnO_2 , V_2O_5 , TiS_2 , Cu_2S , FeS_2 , copper
oxide, copper vanadium oxide, and mixtures thereof, are
also useful as cathode active materials.

To charge such secondary cells, the lithium ions
25 comprising the positive electrode are intercalated into
the carbonaceous anode material or the lithium
intercalation and de-intercalation anode material of the
negative electrode by applying an externally generated
electrical potential to the cell. The applied
30 recharging potential draws the lithium ions from the
cathode active material, through the electrolyte and
into the anode material to saturate it. In the case of
carbon, the resulting Li_xC_6 material can have an x
ranging between 0.1 and 1.0. The cell is then provided
35 with an electrical potential and discharged in a normal

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5 manner.

The above described cathode active materials are formed into a positive electrode by mixing them with one or more of the above described binder materials and conductive diluents. The preferred cathode active 10 mixture thus includes a powdered fluoro-polymer binder present at about 1 to 5 weight percent, a conductive diluent present at about 1 to 5 weight percent and about 90 to 98 weight percent of the cathode active material.

Positive electrodes for incorporation into an 15 electrochemical cell according to the present invention may be prepared by rolling, spreading or pressing the cathode active formulations onto a suitable current collector of any one of the previously described materials suitable for the negative electrode. The 20 preferred current collector material is aluminum. Positive electrodes prepared as described above may be in the form of one or more plates operatively associated with at least one or more plates of a negative electrode, or in the form of a strip wound with a 25 corresponding strip of the negative electrode in a structure similar to a "jellyroll".

In order to prevent internal short circuit conditions, the negative electrode is separated from the positive electrode by a suitable separator material. 30 The separator is of electrically insulative material, and the separator material also is chemically unreactive with the anode and cathode active materials and both chemically unreactive with and insoluble in the electrolyte. In addition, the separator material has a 35 degree of porosity sufficient to allow flow there

5 through of the electrolyte during the electrochemical reaction of the cell. Illustrative separator materials include fabrics woven from fluoropolymeric fibers including polyvinylidene fluoride, polyethylenetetrafluoroethylene, and

10 polyethylenechlorotrifluoroethylene used either alone or laminated with a fluoropolymeric microporous film, non-woven glass, polypropylene, polyethylene, glass fiber materials, ceramics, polytetrafluoroethylene membrane commercially available under the designation

15 ZITEX (Chemplast Inc.), polypropylene membrane commercially available under the designation CELGARD (Celanese Plastic Company, Inc.) and a membrane commercially available under the designation DEXIGLAS (C.H. Dexter, Div., Dexter Corp.).

20 The electrochemical cell of the present invention further includes a nonaqueous, ionically conductive electrolyte which serves as a medium for migration of ions between the negative and positive electrodes during electrochemical reactions of the cell. A suitable

25 electrolyte has an inorganic, ionically conductive salt dissolved in a nonaqueous solvent, and more preferably, the electrolyte includes an ionizable alkali metal salt dissolved in a mixture of aprotic organic solvents comprising a low viscosity solvent and a high

30 permittivity solvent. The inorganic, ionically conductive salt serves as the vehicle for migration of the anode ions to intercalate or react with the cathode active materials. Preferably, the ion forming alkali metal salt is similar to the alkali metal comprising the

35 anode active material.

5 In the case of an anode active material comprising lithium, the alkali metal salt of the electrolyte is a lithium based salt. Known lithium salts that are useful as a vehicle for transport of alkali metal ions between the negative electrode and the positive electrode

10 include LiPF_6 , LiBF_4 , LiAsF_6 , LiSbF_6 , LiClO_4 , LiO_2 , LiAlCl_4 , LiGaCl_4 , $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiSCN , LiO_3SCF_3 , $\text{LiC}_6\text{F}_5\text{SO}_3$, LiO_2CCF_3 , LiSO_6F , $\text{LiB}(\text{C}_6\text{H}_5)_4$, LiCF_3SO_3 , and mixtures thereof.

Low viscosity solvents useful with the present invention include esters, linear and cyclic ethers and dialkyl carbonates such as tetrahydrofuran (THF), methyl acetate (MA), diglyme, triglyme, tetraglyme, dimethyl carbonate (DMC), 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE), 1-ethoxy,2-methoxyethane (EME), ethyl methyl carbonate (EMC), methyl propyl carbonate, ethyl propyl carbonate, diethyl carbonate (DEC), dipropyl carbonate, and mixtures thereof, and high permittivity solvents include cyclic carbonates, cyclic esters and cyclic amides such as propylene carbonate (PC), ethylene carbonate (EC), butylene carbonate, acetonitrile, dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, γ -valerolactone, γ -butyrolactone (GBL), N-methyl-pyrrolidinone (NMP), and mixtures thereof.

30 A preferred electrolyte for a secondary cell according to the present invention comprises a solvent mixture of EC:DMC:EMC:DEC. Most preferred volume percent ranges for the various carbonate solvents include EC in the range of about 20% to about 50%; DMC 35 in the range of about 12% to about 75%; EMC in the range

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5 of about 5% to about 45%; and DEC in the range of about
3% to about 45%. In a preferred form of the present
invention, the electrolyte activating the cell is at
equilibrium with respect to the ratio of DMC:EMC:DEC.
This is important to maintain consistent and reliable
10 cycling characteristics. It is known that due to the
presence of low-potential (anode) materials in a charged
cell, an un-equilibrated mixture of DMC:DEC in the
presence of lithiated graphite ($\text{LiC}_6 \sim 0.01 \text{ V vs Li/Li}^+$)
results in a substantial amount of EMC being formed.
15 When the concentrations of DMC, DEC and EMC change, the
cycling characteristics and temperature rating of the
cell change. Such unpredictability is unacceptable.
This phenomenon is described in detail in U.S. patent
application Serial No. 09/669,936, filed September 26,
20 2000, which is assigned to the assignee of the present
invention and incorporated herein by reference.
Electrolytes containing the quaternary carbonate mixture
of the present invention exhibit freezing points below
-50°C, and lithium ion secondary cells activated with
25 such mixtures have very good cycling behavior at room
temperature as well as very good discharge and
charge/discharge cycling behavior at temperatures below
-40°C.

30 The assembly of the secondary cells described
herein is preferably in the form of a wound element
configuration. That is, the fabricated negative
electrode, positive electrode and separator are wound
together in a "jellyroll" type configuration or "wound
element cell stack" such that the negative electrode is
35 on the outside of the roll to make electrical contact

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5 with the cell case in a case-negative configuration. Using suitable top and bottom insulators, the wound cell stack is inserted into a metallic case of a suitable size dimension. The metallic case may comprise materials such as stainless steel, mild steel,
10 nickel-plated mild steel, titanium, tantalum or aluminum, but not limited thereto, so long as the metallic material is compatible for use with the other cell components.

15 The cell header comprises a metallic disc-shaped body with a first hole to accommodate a glass-to-metal seal/terminal pin feedthrough and a second hole for electrolyte filling. The glass used is of a corrosion resistant type having up to about 50% by weight silicon such as CABAL 12, TA 23, FUSITE 425 or FUSITE 435. The
20 positive terminal pin feedthrough preferably comprises titanium although molybdenum, aluminum, nickel alloy, or stainless steel can also be used. The cell header is typically of a material similar to that of the case. The positive terminal pin supported in the
25 glass-to-metal seal is, in turn, supported by the header, which is welded to the case containing the electrode stack. The cell is thereafter filled with the electrolyte solution described hereinabove and hermetically sealed such as by close-welding a stainless
30 steel ball over the fill hole, but not limited thereto.

35 The above assembly describes a case-negative cell, which is the preferred construction of the exemplary secondary cell of the present invention. As is well known to those skilled in the art, the present secondary electrochemical systems can also be constructed in case-

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5 positive configuration.

It is appreciated that various modifications to the
inventive concepts described herein may be apparent to
those of ordinary skill in the art without departing
from the spirit and scope of the present invention as
10 defined by the appended claims.

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